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(54) Purple diamond and method of producing the same.

(57) A purple diamond characterized in that the absorption coefficient of the Ib type nitrogen at 500 nm is 0.2 -2 cm^{-1}, the absorption coefficient of the N-V center at an absorption peak of 570 nm is 0.3 - 10 cm^{-1}, and the absorption coefficients of the GR1 center, H2 center, H3 center and H4 center are less than 0.2 cm^{-1} in the visible region. A method of producing a purple diamond characterized by using an Ib type artificial synthetic diamond crystal wherein the Ib type nitrogen content in the crystal is within the range of 8×10^{17} - 1.4×10^{19} atoms/cm^3, subjecting the diamonds crystal to an electron beam irradiation by 5×10^{16} - 2×10^{18} electrons/cm^2 at 2 - 4 MeV, and annealing it in a vacuum of less than 10^{-2} Torr at a temperature of 800 - 1100 °C for more than 25 hours.

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Purple Diamond and Method of Producing the Same

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a purple diamond suitable, for example, for ornamental purposes and a method of producing the same.

Description of the Background

To obtain a colored diamond, it has been usual practice to irradiate a natural diamond with an electron beam and then anneal the same under a vacuum atmosphere, so as to form a color center.

A color center is formed when a nitrogen atom in a crystal and a lattice defect formed by the irradiation of an electron beam are combined with each other by the action of annealing. Further, a lattice defect alone is also effective in forming a colored diamond. Further, the type of the color center is determined by the manner in which nitrogen atoms aggregate together. The relation between color centers and colors is shown in Table 1.

Table 1

Item / Center Name	State of Combination in Color Center	Color of Color Center
H3 Center	A pair of nitrogen atoms and a lattice defect	Yellow
H4 Center	Two pairs of nitrogen atoms and a lattice defect	Yellow
N-V Center	An isolated nitrogen atom and a lattice defect	Purple
GR1 Center	A lattice defect	Bluish green
N3 Center	Three nitrogen atoms (naturally occurring)	Light yellow

For the methods of forming the color centers listed in Table 1 and their characteristics, refer to "Optical absorption and luminescence in diamonds," Reports on Progress Physics, John Walker, Vol. 42, 1979. Further, the true colors exhibited by colored diamonds are the colors indicated in Table 1 superposed on the intrinsic colors of natural rough diamonds.

The intrinsic colors of natural rough diamonds are classified as shown in Table 2.

Table 2

Classification of Diamonds / Item	Color of Rough Stone	Configuration in which Nitrogen Exists: Isolated nitrogen atoms	1 pair of nitrogen atoms	2 pairs of nitrogen atoms	3 nitrogen atoms	Proportion Occurring in Nature
IIa	Transparent colorless	Absent	Absent	Absent	Absent	1 %
Ia	Transparent colorless	Absent	Present	Present	Absent	10 %
	Light yellow	Absent	Present	Present	Few	90 %
	Yellow	Present	Present	Present	Present	
	Brown	Many	Present	Present	Many	
IIb	Blue	Absent (containing B)	Absent	Absent	Absent	approximately 0 %
Ib	Clear yellow	Present	Absent	Absent	Absent	0.2 %

As is obvious from Table 2 and Table 1, those rough stones are colored effectively by making a color center indicated in Table 1 in type IIa or Ia diamonds which are transparent colorless or light yellow. These rough stones either do not have nitrogen at all or have 1 or 2 pairs of nitrogen atoms. Thus, it follows that coloration is effective for only two colors which follow:

(1) Bluish green (based on the GR1 center formed solely by electron beam irradiation)

(2) Yellow (based on the H3 and H4 centers formed by electron beam irradiation and annealing).

From the above observation, we have concluded that a diamonds which exhibits purple developed by the N-V center can hardly be produced from natural rough stones and that a purple diamond which induces a transparent sensation in the mind and whose color is brilliant cannot be produced from natural rough stones. Further, since the Ib type rough stone containing isolated type nitrogen alone for production of the N-V center is present in as low as 0.2 % of natural rough stones, it is very difficult to obtain such rough stone itself.

Thus, we conceived the idea of using an Ib type artificial synthetic diamond which contains 100 % isolated nitrogen. In addition, a method of producing the N-V center by electron beam irradiation and annealing is described in A.T. Collins, Journal of Physics C, Solid State Physics, 16 (pp. 2177-2181, 1983). However, to put a colored diamond to ornamental use, it should induces a transparent sensation in the mind and its color should be brilliant, a problem which has not been solved.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a purple diamond which induces a transparent sensation in the mind and whose color is brilliant and a method of mass-producing the same.

A purple diamond according to the present invention is characterized in that the absorption coefficient of the Ib type nitrogen at 500 nm is 0.2 - 2 cm^{-1}, the absorption coefficient of the N-V center at an absorption peak of 570 nm is 0.3 - 10 cm^{-1}, and the absorption coefficients of the GR1 center, H2 center, H3 center and H4 center are less than 0.2 cm^{-1} in the visible region.

A method of producing a purple diamond according to the invention used an Ib type artificial synthetic diamond crystal wherein the Ib type nitrogen content is within the range of 8×10^{17} - 1.4×10^{19} atoms/cm^3. And it is characterized by subjecting said diamond crystal to an electron beam irradiation of 5×10^{16} - 2×10^{18} electrons/cm^2 at 2 - 4 MeV, followed by annealing in a vacuum of less than 10^{-2} Torr at a temperature of 800 -1100 °C for more than 25 hours.

Our Purple Diamond

The transparent sensation depends on the absorption coefficient of the N-V center and on the absorption coefficient of the Ib type nitrogen, and to induce a transparent sensation in the mind, it is important that this value has to be within said range. On the other hand, in order to ensure the color brilliance of the diamonds, it is important that the absorption coefficients of the other color centers have to be less than 0.2 cm^{-1} in the visible region in addition to the restriction as to the absorption coefficients of said N-V center and Ib type nitrogen.

(A) On absorption Coefficient of N-V Center:

In the N-V center absorption occurs from 500 nm to 640 nm, the peak value being 570 nm. Therefore, the center color of absorption is yellow. As a result of this absorption, the crystals exhibit a complementary color, purple. This absorption plays an important role in determining the color of a purple diamond according to the invention.

The transparent sensation is an important factor in ornamental use. This correlates to absorption coefficient such that the transparent sensation is lost when the absorption coefficient exceeds 10 cm^{-1}. On the other hand, for an absorption coefficient of less than 0.3 cm^{-1}, the purple disappears, giving place to the yellow which is the intrinsic color of the rough stone.

(B) On Absorption Coefficient of Type Ib Nitrogen:

In the case of type Ib nitrogen, the absorption occurs at 550 nm. As a wavelength decreases, the absorption coefficient increases and becomes almost equal to the infinity at 400 nm. The range in which absorption increases lies above 500 nm, where blue, indigo and purple colors are absorbed, with the crystals exhibiting a complementary color, yellow. If this yellow is light, it mixes with purple, exhibiting a clear purple color, inducing a transparent sensation in the mind. This effect will not take place if the absorption coefficient at 500 nm is less than 0.2 cm^{-1}. If it exceeds 2 cm^{-1}, the yellow is too dark for the crystals to induce a transparent sensation in the mind and predominates over purple; purple is not longer exhibited.

(C) On Absorption Coefficient Associated with Other Types of Absorption:

When other types of absorption (by the GR1 center, H2 center, H3 center and H4 center) take place in the visible region, the purple becomes turbid, decreasing the brilliant sensation. To maintain the brilliant sensation, it is important that the absorption coefficient be less than 0.2 cm^{-1}. Absorption peaks representative of other types of absorption taking place in the visible region include those from the GR1 center where absorption appears at 550 - 740 nm and the H2 center where absorption appears at 650 - 990 nm. Since these centers absorb colors which lie around red, excessively high absorption coefficients would cause green, which is a complementary color, to mix with purple, decreasing the brilliant sensation.

On Production Method

(A) Use of Ib type artificial synthetic diamonds:

In the case of natural diamonds, since various forms of nitrogen atoms are contained, annealing will provide a plurality of type of color centers. Therefore, it is very difficult to prepare a rough stone which contains the N-V center alone by using a natural diamond.

Ib type artificial synthetic diamonds contain 100 % isolated type nitrogen atoms. For this reason, if an artificial synthetic diamond is used, a rough stone which contains the N-V center alone can be easily produced. In this case, a diamond synthesized by the temperature gradient method contains a less amount of bulk-like inclusions than does a diamond synthesized by the film growth method, resulting in large-sized crystals, a fact which is desirable.

(B) On Nitrogen Content:

The factor which is most closely correlated to the absorption coefficient of the N-V center and to the absorption coefficient of the Ib type nitrogen is the nitrogen content. If the content is less than 8×10^{17} atoms/cm^3, the absorption coefficient of the N-V center at 570 nm will be 0.2 cm^{-1} or the absorption coefficient of the Ib type nitrogen at 500 nm will be less than 0.3 cm^{-1}. Further, if the content exceeds 1.4×10^{19} atoms/cm^3, the absorption coefficient of the N-V center will exceed 2 cm^{-1} or the absorption coefficient of the Ib type nitrogen will exceed 10 cm^{-1}.

(C) On Electron Beam Irradiation:

Uniform formation of lattice defects by electron beam irradiation is essential for uniform production of the N-V center throughout the crystals. Under the condition of irradiation with less than 5×10^{15} electrons/cm^2 at 2 MeV, the lattice defect concentration will be decreased in some of the crystal. Further, above 4 MeV, there will be a possibility of the inclusions being irradiated. With an irradiation dose which exceeds 2×10^{18} electrons/cm^2, the defect concentration will be too high, raising a problem that the GR1 center cannot be removed or that the H2 center begins to form. In this case, there will be a high degree of absorption in the visible region due to other than the N-V center and Ib type nitrogen.

(D) On Annealing:

More than 25 hours of annealing satisfactorily eliminates the GR1 center produced by electron beam irradiation and ensures satisfactory combination between the Ib type nitrogen and lattice defects. With less than 25 hours of annealing, however, said effects cannot be attained to the fullest extent. Further, with a vacuum which exceeds 10^{-2} Torr, graphitization of diamond surface will occur. If the annealing temperature is less than 800°C, the GR1 center cannot be fully removed, while if it exceeds 1100°C, the N-V center begins to be destroyed and the purple is lightened.

According to the invention, a purple diamond which induces a transparent sensation in the mind and whose color is brilliant can be obtained. Furthermore, according to a method of producing a purple diamond, since a purple diamond is obtained by the process characteristic of the invention by using an artificial synthetic diamond, it is easy to procure the necessary rough stone and hence purple diamonds can be mass-produced.

Examples

Example 1

Seven Ib type artificial synthetic diamonds (whose nitrogen content was 4×10^{17} to 4×10^{19} atoms/cm^3) synthesized by the temperature gradient method were subjected to electron beam irradiation using 1×10^{16} to 2×10^{19} electrons/cm^2 at 3 MeV. Subsequently, they were subjected to 30 hours of annealing in a vacuum of 10^{-3} Torr at 900°C.

The diamonds obtained were tested for the absorption coefficient of the N-V center, Ib type nitrogen, GR1 and H2 centers by using an ultraviolet visible spectroscope.

Further, said samples were brilliant-cut into 0.5 -0.6 carat/piece. To evaluate them as to their ornamental use, 100 randomly selected women aged 18 - 65 were requested to observe said sample and information on the following subjects was gathered through this questionnaire. The result is shown in Table 3.

(Subjects to be asked in the questionnaire)

(1) Does it induce a transparent sensation in the mind?
(2) Is the color brilliant?
(3) Does it have an ornamental value?

Table 3

Sample No.		1	2	3	4	5	6	7
Ultraviolet	N-V center absorption coefficient (cm^{-1})	0.4	0.1	0.3	0.6	10	8	15
visible	Ib type nitrogen absorption coefficient (cm^{-1})	0.15	0.2	0.2	0.3	2	3	2
spectroscopic analysis	Other-center absorption coefficient (cm^{-1})	Approximately 0	Approximately 0	Approximately 0	Approximately 0	0.1 or less	Approximately 0	0.1 or less
Nitrogen concentration of rough stone ($atoms/cm^3$)		8×10^{17}	4×10^{17}	8×10^{17}	1.7×10^{18}	1.4×10^{19}	5×10^{19}	3×10^{19}
Electron beam irradiation dose ($electrons/cm^2$)		3×10^{16}	2×10^{18}	5×10^{15}	1×10^{18}	2×10^{18}	5×10^{16}	2×10^{18}
Result	Transparent sensation (persons)	100	100	100	100	80	40	10
of	Color brilliantness (persons)	52	30	90	100	85	10	20
questionnaire	Ornamental value (persons)	48	30	90	100	75	18	5
		Control	Control	Example	Example	Example	Control	Control

In addition, the result of the questionnaire shown in Table 3 indicates the number of persons who answered "Yes".

Example 2

Three Ib type synthetic diamonds (whose nitrogen content was 2×10^{18} atoms/cm^3) synthesized by the temperature gradient method were subjected to electron beam irradiation using 2×10^{18} to 1×10^{19} electrons/cm^2 at 3 MeV. Subsequently, they were subjected to 10 - 40 hours of annealing in a vacuum of 10^{-4} Torr at 1100°C.

The samples obtained were tested for the absorption coefficient of the N-V center, Ib type nitrogen, GR1 center and H2 center by using an ultraviolet visible spectroscope.

Further, said samples were brilliant-cut into 0.8 -1.2 carats/piece. To evaluate them as to their ornamental use, a questionnaire was conducted in the same manner as in Example 1, and the result is shown in Table 4.

Table 4

Sample No.		1	2	3
Ultraviolet visible spectroscopic analysis (cm^{-1})	N-V center absorption coefficient (cm^{-1})	0.7	0.6	0.7
	Ib type nitrogen absorption coefficient (cm^{-1})	0.3	0.3	0.3
	Other-center absorption coefficient (cm^{-1})	Approximately 0	0.3	3.5
Electron beam irradiation dose (electrons/cm^2)		2x10^{18}	2x10^{18}	1x10^{19}
Annealing time (hours)		25	10	40
Result of questionnaire	Transparent sensation (persons)	100	98	0
	Color brilliantness (persons)	100	55	5
	Ornamental value (persons)	100	45	0
		Example	Control	Control

In addition, the result of the questionnaire shown in Table 4 indicates the number of persons who answered "Yes".

Although the present invention has been described in detail, it is clearly understood that the same is by way of example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A purple diamond characterized in that the absorption coefficient of the Ib type nitrogen at 500 nm is 0.2 - 2 cm^{-1}, the absorption coefficient of the N-V center at an absorption peak of 570 nm is 0.3 - 10 cm^{-1}, and the absorption coefficients of the GR1 center, H2 center, H3 center and H4 center are less than 0.2 cm^{-1} in the visible region.

2. A method of producing a purple diamond characterized by using an Ib type artificial synthetic diamond crystal wherein the Ib type nitrogen content in the crystal is within the range of 8×10^{17} - 1.4×10^{19} atoms/cm^3,
subjecting said diamonds crystal to an electron beam irradiation by 5×10^{16} - 2×10^{18} electrons/cm^2 at 2 -4 MeV, and
annealing it in a vacuum of less than 10^{-2} Torr at a temperature of 800 - 1100°C for more than 25 hours.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 11 8998

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	EP-A-0 275 063 (SUMITOMO ELECTRIC INDUSTRIES LTD) * Page 3, lines 20-25; figure 2; page 4, lines 56-58; page 5, lines 1-39; examples 1,4; claims 7,8 * ---	1,2	C 30 B 33/00 C 30 B 29/04 B 01 J 19/08 A 44 C 17/00 B 28 D 5/00
Y	US-A-2 945 793 (DUGDALE) * Column 2, lines 25-38,66-71; claims 1,2 * ---	1,2	
Y	US-A-2 998 365 (CUSTERS) * Column 3, lines 37-41; column 5, lines 57-61 * ---	1,2	
Y	J. PHYS. C: SOLID ST. PHYS., vol. 13, 1980, pages 2641-2650, The Institute of Physics, GB; A.T.COLLINS: "Vacancy enhanced aggregation of nitrogen in diamond" * Page 2644, section 3.1 and figure 2 * ---	1,2	
A	EP-A-0 014 528 (DE BEERS INDUSTRIAL DIAMOND DIVISION) * Claims 1,3,4,7 * ---	2	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	FR-A-2 456 766 (VSESOJUZNY NAUCHNO-ISSLEDOVATELSKY INSTITUT SINTEZA MINERALNOGO SYRYA & RADIOTECHNICHESKY INSTITUT AKADEMII NAUK SSSR) * Page 2, lines 21-30 * ---	2	A 44 C B 01 J C 30 B H 01 S
A	WO-A-8 603 347 (HUGHES AIRCRAFT CO.) * Page 13, lines 24-35; page 14, lines 1-13 * --- -/-	2	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-02-1989	COOK S.D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 174 380 (STRONG et al.) * Column 2, lines 54-68 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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